

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 6 :</b> <b>A23F 5/16</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/23890</b> <b>(43) International Publication Date:</b> 20 May 1999 (20.05.99)
<b>(21) International Application Number:</b> PCT/EP98/06760 <b>(22) International Filing Date:</b> 24 October 1998 (24.10.98) <b>(30) Priority Data:</b> MI97A002496 7 November 1997 (07.11.97) IT <b>(71) Applicant (for all designated States except US):</b> DEMUS S.P.A. [IT/IT]; Via G. & S. Caboto, 31, I-34147 Trieste (IT). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> FABIAN, Massimiliano [IT/IT]; Demus S.p.A., Via G. & S. Caboto, 31, I-34147 Trieste (IT). <b>(74) Agents:</b> FERRAILOLO, Ruggero et al.; Via Napo Torriani, 10, I-20124 Milano (IT).	<b>(81) Designated States:</b> BR, CA, CN, ID, JP, MX, SG, SI, US, VN, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>	
<b>(54) Title:</b> PROCESS FOR REMOVING MICOTOXINS FROM A LOAD OF GREEN COFFEE  <b>(57) Abstract</b>  Green coffee is introduced into a container where it is subjected to continuous mixing in temperature conditions ranging between environment and values close to 120 °C and water vapour is introduced into said container until the single beans of coffee have become porous and permeable; micotoxins are removed by extraction with a solvent in an acid environment obtained with a given acid or with a buffer solution with a given acid pH.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Process for removing micotoxins from a load of green coffee.

The present invention concerns a process for removing micotoxins from a load of green coffee, intending micotoxins in this case at least those micotoxins known as ochratoxins and aflatoxins that may be present in green coffee. One of the purposes of this process is to remove the micotoxins though maintaining the quantity of caffeine within the values of a non decaffeinated coffee. It is well known that the quantities of these micotoxins in coffee are very small in an absolute sense (for instance only a few - ppb - parts per billion, that is mg/ton) and that their presence may depend on the geographic area in which coffee grows, on possible unfavourable weather conditions and on possible negligence in storage and handling.

On the 13<sup>th</sup> May 1996 the applicant submitted the patent application MI 96 A 000960 for an industrial process suitable to removing the above mentioned micotoxins from green coffee, said process essentially comprising the following stages:

- a) introducing a load of green coffee containing micotoxins into a container in which the coffee will preferably be subjected to continuous mixing at temperatures ranging between environmental and values about 105°C;
- b) introducing water vapour into the container where it is kept until the coffee beans have become porous and permeable;
- c) introducing into the container of a solvent suited to removing

waxes and micotoxins and extraction of the solvent as soon as it has removed the waxes and most of the micotoxins from the coffee;

d) recovering the solvent and separation from the latter of the micotoxins contained therein.

5 A first alternative to the above said stage c ) is stage:

c') introducing into the container a solvent saturated with caffeine leaving long enough to remove the totality of the micotoxins.

In a second alternative, the process contemplates the repetition of the stage c ) in order to increase the level of removal of the micotoxins.

10 A first drawback of the above said process lies in the difficulty, from a plant viewpoint, of operating with a solvent saturated with caffeine.

A second drawback is given by the fact that to saturate the solvent with caffeine large quantities of the latter are required.

15 A further drawback of said process is given by the fact that the repetition of stage c ) in order to increase to a higher level the removal of the micotoxins causes the removal of further quantities of caffeine from the coffee.

20 The applicant has furthered experiments until finding out that, by creating an acid environment obtained by means of a chosen acid or buffer solution with a given acid pH, in some of the process stages the removal of micotoxins is increased, while at the same time, the removal of caffeine is reduced compared to the known process. Note that the known process takes place in a neutral

environment.

The suitable acid environment for the above results is to be chosen by the operator between pH = 7 and pH = 2 as a function of the contact time between coffee and the acid mixed with the solvent used or else the contact time between  
5 the coffee and the buffer solution as a function of the temperature at which said contacts takes place.

Such an acid environment can be achieved as follows:

- introducing into the process an acid mixed with the solvent for the removal of micotoxins or, as an alternative;
- 10 - introducing into the process a buffer solution with an acid pH and leave it in contact with the coffee for the required time;
- later discharge said buffer solution and introduce the solvent for the removal of the micotoxins.

On the basis of the results of the further experiments the process that is  
15 the subject of the present patent application comprises the following known stages:

- a) introducing a load of green coffee containing micotoxins into a container in which the coffee is preferably subjected to continuous mixing in temperature conditions ranging between environment and values about 105°C;
  - b) introducing into the container water vapour to be kept there for the  
20 time required for the coffee beans to become porous and permeable;
- and newly includes, as characterized in the claims, the following

subsequent stages:

- c) introducing into the container a quantity of solvent equal to at least 50% of the weight of the coffee, the solvent containing a suitable quantity of acid, and leaving it in contact with the coffee for at least 10' at a temperature that ranges  
5 from environment to about 105° C, such higher value being raised upto 120°C when using kinds of solvent adapted to it;

This stage c) may be repeated until most of the micotoxins have been removed. Note that "suitable quantity of acid" means that amount as chosen by the operator depending on the contact time between the coffee and the acid mixed with  
10 the solvent and on the temperature at which the removal takes place;

- d) recovering the micotoxin removal material and separating the micotoxins contained therein.

An alternative to the above stage ( c ) is a stage:

- c') introducing a buffer solution featuring a chosen acid pH, the acidity  
15 being a function of the contact time of the same buffer solution with the coffee and as a function of the temperature at which this stage of the process takes place, the buffer solution being a variable quantity between 50 and 200% of the weight of the coffee load; the said contact time ranging between 10 and 60 minutes;

d') discharging the buffer solution:

- e) introducing into the container a quantity of solvent, equal to at least  
20 50% of the weight of the coffee load, and then extract it after the removal of the

grater part of the micotoxins from the coffee;

f) recovering the micotoxin removal solvent and separating the micotoxins contained therein.

A further improvement defined by the experiments is that of adding to  
5 the water vapour in the stage (b) a quantity of water ranging between 5 and 50% of the weight of the coffee load at a temperature ranging between environment and a value close to 90°C so that the coffee beans become porous and permeable more rapidly.

In order to better understand the invention some examples of  
10 embodiment of the process are described herebelow.

#### EXAMPLE 1

Description of a process in which the removal stage takes place at environmental temperature and the acid is previously mixed with the solvent:

- a) as defined above;
- 15 b) as defined above;
- c) introducing into the container a quantity of dichloro methane equal to at least 50% of the weight of the coffee load, the dichloro methane containing 2% of formic acid, and leaving it in contact with the coffee for 30' this stage being repeatable until most of the micotoxins have been removed.
- 20 d) Recovering the micotoxin removal material and separating the micotoxins contained therein.

## EXAMPLE 2

Description of a process in which a container brought to environmental temperature is previously filled with an acid pH buffer solution:

- a) as defined above;
- 5 b) as defined above;
- c) introducing into the container a quantity of phosphate buffer solution with pH 4, ranging between 50 and 200% of the weight of the coffee load, and leaving it in contact with the coffee for 15'.
- d) Discharging the buffer solution;
- 10 e) Introducing into the container dichloro methane, in a quantity equal to at least 50% of the weight of the coffee load, in order to remove the micotoxins and extracting the solvent after the removal of most of the micotoxins from the coffee;
- f) Recovering the solvent and separating the micotoxins contained
- 15 therein.



## Claims

1. Process for removing micotoxins from a load of green coffee in which the coffee is introduced into a container where it is subjected to continuous mixing in temperature conditions ranging between environment and a value of about 105°C and water vapour is introduced into the container until the single beans of coffee have become porous and permeable, **characterized** in that the stages for removing micotoxins are made to take place in an acid environment obtained by means of a chosen acid or an acid pH buffer solution and at a temperature ranging between environment and 120°C.
2. Process according to claim 1 characterized in that the said acid environment will be chosen between  $\text{pH} = 7$  and  $\text{pH} = 2$  as a function of the contact time between the coffee and the chosen acid mixed with the solvent or the contact time between the coffee and the chosen buffer solution as a function of the temperature at which such contacts take place.
3. Process according to claims 1 and 2 characterized in that it includes the following stages:
- introducing into the container a quantity of solvent equal to at least 50% of the weight of the coffee load, the solvent containing a suitable quantity of acid, and leaving it in contact with the coffee for a time of at least 10', such a stage being repeatable until the greater part of the micotoxins are removed;
  - recovering the micotoxin removal material and separating the

micotoxins contained therein.

4. Process according to claims 1 and 2 characterized in that it includes the following stages:

- introducing a quantity of acid pH buffer solution at the chosen  
5 acidity level ranging between 50 and 200% of the weight of the coffee load and leaving it in contact with the coffee for a time ranging between 10' and 60';
- discharging the buffer solution;
- introducing into the container a quantity of solvent equal to at least  
50% of the weight of the coffee load and extracting the same after the removal of  
10 the greater part of the micotoxins from the coffee;
- recovering the micotoxin removal solvent and separating the  
micotoxins contained therein.

5. Process according to the previous claims characterized in that in stage (b) a quantity of water ranging between 5 and 50% of the coffee load may be  
15 added to the water vapour at a temperature ranging between environment and a value close to 90°C.

# INTERNATIONAL SEARCH REPORT

Interr. Appl. No.  
PCT/EP 98/06760

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A23F5/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A23F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 688 638 A (K. LENDRICH) 20 September 1930 see claims 1,5; example ---	1
A	CH 568 719 A (HACO) 14 November 1975 see column 2, line 22 - column 3, line 31; claim 1 ---	1,3
A,P	WO 97 42831 A (DEMUS) 20 November 1997 cited in the application see claims 1-4 --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

8 March 1999

Date of mailing of the international search report

07/04/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Desmedt, G

# INTERNATIONAL SEARCH REPORT

Int. onal Application No

PCT/EP 98/06760

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	H. TERADA : "Liquid chromatographic determination of ochratoxin A in coffee beans and coffee products" JOURNAL OF THE ASSOCIATION OF OFFICIAL ANALYTICAL CHEMISTS, vol. 69, no. 6, 1986, pages 960-964, XP002095819 see page 960, column 2 ---	1
A	US 5 112 637 A (R. HRON) 12 May 1992 see claims 1,20,21; example 2; table II ---	1
A	DE 26 39 066 A (HAG) 2 March 1978 see claims 1-10 ---	1,3
A	US 5 288 511 A (P. KAZLAS) 22 February 1994 see claim 1; example ---	1,3
A	EP 0 158 381 A (DOUWE EGBERTS) 16 October 1985 see claim 1 -----	1,3

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/EP 98/06760

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 688638 A	20-09-1930	NONE	
CH 568719 A	14-11-1975	NONE	
WO 9742831 A	20-11-1997	IT MI960960 A	13-11-1997
US 5112637 A	12-05-1992	NONE	
DE 2639066 A	02-03-1978	CH 622682 A	30-04-1981
		DD 127467 A	28-09-1977
		FR 2362592 A	24-03-1978
		US 4168324 A	18-09-1979
US 5288511 A	22-02-1994	AT 140855 T	15-08-1996
		AU 8516891 A	17-03-1992
		CA 2088051 A,C	24-02-1992
		DE 69121206 D	05-09-1996
		DE 69121206 T	05-12-1996
		EP 0547119 A	23-06-1993
		WO 9203061 A	05-03-1992
EP 158381 A	16-10-1985	NL 8400759 A	01-10-1985
		AT 36803 T	15-09-1988
		CA 1240550 A	16-08-1988
		DE 3564649 A	06-10-1988
		DK 109185 A,B,	10-09-1985
		JP 1358633 C	13-01-1987
		JP 60259145 A	21-12-1985
		JP 61022934 B	03-06-1986